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Integration of Damage Mechanism Review with Process Hazard Analyses

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Abstract

Significant releases of highly toxic and flammable materials have occurred in various industries as a direct result of corrosion effects and other damage mechanisms. Examples of such events can readily be found in petroleum refineries and ammonia refrigeration facilities. Understanding and identification of these damage mechanisms and locations of susceptibility play a critical role in limiting the likelihood of loss of primary containment, which can have serious safety consequences.

Process Hazard Analysis (PHA) provides a thorough and efficient method for systemically reviewing complex systems for safety concerns. A commonly applied PHA method is the Guide-Word Style Hazard and Operability (HAZOP) approach, which breaks complex systems into focused sections called nodes. This methodology can be augmented to systematically address the effects of various damage mechanisms. Possibility of corrosion and other damage mechanisms can be included in each node through the addition of a new deviation dedicated to these phenomena. The PHA Team with the help of a subject matter expert reviews the various mechanisms unique to a particular node that can cause loss of integrity.

PHA discussions of damage mechanisms should address normal and abnormal operating conditions. The timing of progression of damage mechanism effects and established methods for discovering the damage (detection safeguard) should be explicitly noted. It is important to note that such discussions require participation of experts in metallurgy, corrosion mechanisms, inspection techniques, and process chemistry. The proposed method has been applied successfully in identifying potential vulnerabilities and improvements to minimize the risks associated with corrosion. Specific examples are shown from actual studies addressing systematic analysis of damage mechanisms and the lessons learned from those studies.

1. Introduction and Background

Major events within the past several years have resulted from damage mechanisms that progressed to loss of containment incidents[1]. Damage mechanisms can occur as both slow and fast acting types and appear in a multitude of forms. As a result of several of these incidents, investigating agencies such as the Chemical Safety Board (CSB) have issued incident reports documenting that the Process Hazard Analysis must be used as a tool to identify and establish the risks associated with damage mechanisms. For example, as part of the CSB's investigation of the Tesoro Anacortes incident in 2010 [Reference 1], the board issued Recommendation 2010-08-I-WA-4, which includes the following statement:

> *"iii. Documented damage mechanism hazard review conducted by a diverse team of qualified personnel. This review shall be an integral part of the Process Hazard Analysis cycle and shall be conducted on all PSM-covered process piping circuits and process equipment. The damage mechanism hazard review shall identify potential process damage mechanisms and consequences of failure, and shall ensure effective safeguards are in place to control hazards presented by those damage mechanisms. Require the analysis and incorporation of applicable industry best practices and inherently safer design to the greatest extent feasible into this review; and . . ."*

Additionally, CSB's investigation of the Chevron Richmond Refinery Incident in 2012 [Reference 2], included the following recommendation:

> *2012-03-CA-9 "Revise the California Code of Regulations, Title 8, Section 5189, Process Safety Management of Acutely Hazardous Materials, to require improvements to mechanical integrity and process hazard analysis programs for all California oil refineries. These improvements shall include engaging a diverse team of qualified personnel to perform a documented damage mechanism hazard review. This review shall be an integral part of the Process Hazard Analysis cycle and shall be conducted on all PSM-covered process piping circuits and process equipment. The damage mechanism hazard review shall identify potential process damage mechanisms and consequences of failure, and shall ensure safeguards are in place to control hazards presented by those damage mechanisms. Require the analysis and incorporation of applicable industry best practices and inherently safety systems to the greatest extent feasible into this review."*

As a result of the latter event and subsequent recommendations from the CSB, an Interagency Working Group was formed in California that put forward the following recommendations in their report [Reference 3] addressing oil refineries:

[1] The CSB lists 125 significant petroleum refinery incidents in 2012 as part of Appendix A of its Regulatory Report on the Chevron Richmond Refinery incident [Reference 2]. Many of these events were associated with system integrity failures.

Recommendation F.3.1.c

"*Require Refineries to Conduct Damage Mechanism Hazard Reviews*
Current PSM and CalARP programs require facilities to include a Mechanical Integrity Process Safety element. The Mechanical Integrity element requires facilities to ensure the mechanical integrity of processes through purchasing of new or replacement equipment, performing inspections, and other actions. But current regulation does not require that an important type of analysis, known as damage mechanism hazard review, be conducted at refineries. This review analyzes risks presented by all known process failure mechanisms at refineries, including corrosion, stress cracking, damage from high temperatures, and mechanical or metallurgical assisted degradation, and should be included as part of the Mechanical Integrity element. In addition, the results of the damage mechanism hazard reviews, as well as other Mechanical Integrity reviews currently required, should be explicitly incorporated in the information provided to process hazard analysis teams at refineries, and to agencies overseeing refinery safety. Current regulation (both the Contra Costa County ISO and Title 8 PSM regulations) requires that these results be used by process hazard analysis teams at refineries, and these teams should be required to include a corrosion engineer or other professional with the expertise to understand this information."

The California Governor's Office of Emergency Services (CalOES) and California's Occupational Health and Safety Administration (CalOSHA) are currently in the process of updating the California Accidental Release Prevention Program (CalARP) and PSM regulations [References 4 and 5], in which the term Damage Mechanism Review (DMR) is defined under the Mechanical Integrity section of the regulations.

The list of DMR requirements in the proposed regulations effectively covers all the issues that one could raise related to the impact of damage mechanisms on process piping and equipment. Clearly they must be addressed systematically and thoroughly to ensure that all potential damage scenarios are identified and addressed. Process Hazard Analysis (PHA), as it is practiced today, provides one such methodology. In this article, the various damage mechanisms that may threaten integrity of piping and equipment are discussed first. A PHA-based methodology that has been successfully applied is presented along with example cases.

2. Typical Damage Mechanisms in the Process Industry

Typical damage mechanisms in refining and hydrocarbon processing can be found in API 571 [Reference 6]. There are more than 70 damage mechanisms listed in this publication, which serves as a good starting point to gain an understanding of the damage mechanisms that may occur in the petroleum industry. It must be noted that API 571 is not comprehensive of all damage mechanisms. The damage mechanisms identified in API 571 are not unique to refining or hydrocarbon processing and all of them can be found in other process industries. API 571 provides a definition for each damage mechanism, provides visual depictions of each mechanism, discusses the materials affected, and explains the Nondestructive Evaluation (NDE) techniques that may be used to discover the presence of a damage mechanism. There are many other publications and reference books that define corrosion mechanisms specific to process industries.

3. Applying PHA Methodology to Address Damage Mechanisms

In the RMP and PSM regulations, it is stated that Process Hazard Analysis shall address "The hazards of the process" [e.g., see 40 CFR 68.67 of Reference 7]. Identifying and addressing the hazards of the process is an important step in risk reduction application within the chemical processing industry. This effort not only ensures that a site complies with the regulatory requirements, but provides owners with a method of reducing the potential for high severity consequences. Therefore, since most chemical process systems are susceptible to various forms of damage mechanisms, the PHA process can play an essential role in establishing these hazards and their associated risks.

A Process Hazard Analysis (PHA) is a risk assessment used for identifying potential hazards associated with chemical processing systems and associated operations. Several methodologies exists for conducting a PHA. The specific methodology that we have used to identify and address damage mechanism hazards is the Guide-Word Style Hazard and Operability (HAZOP) study approach.

3.1 Key Attributes of Guide-Word Style HAZOP

A HAZOP study is a systematic and methodical review of system design and operation. The study uses an investigative technique known as the "guide-word method" [Reference 8]. This method employs a pre-selected set of parameters and guidewords to facilitate a thought process for identifying potentially hazardous situations or operating problems. Guide-word methodology is widely accepted by the process industry and governmental agencies as the most convenient systematic method for identifying hazardous conditions in process systems.

It is important to note that a HAZOP is conducted by a team of experts in a set of brainstorming sessions which are led by a facilitator. Typically, the discussions are recorded by a scribe using a standardized spreadsheet. The team of experts typically represents engineering, operations, maintenance, safety and health, and management. Other experts are often invited on an as needed basis when addressing specialized topics such as electrical power distribution, rotating equipment, and other special issues.

The HAZOP methodology is based on the premise that each component or segment of a system has a specific design intent, and a deviation from this intent may lead to a hazardous condition. For example, a distillation tower is designed to contain a certain amount of fluid. Maintaining the liquid level within safe limits is a design intent of operating the tower. If the tower is overfilled (a deviation from the design intent) liquid may enter the vapor lines and may lead to adverse consequences downstream. If the vessel level drops below a certain level (also a deviation), pump cavitation and operational problems may be experienced. Corrosion and other damage mechanisms can be regarded as a deviation that may have long or short term effects.

In a HAZOP study, the system is divided into nodes (segments, or process sections). The nodes may be selected based on the conditions of the effluents in the system. Typically, nodes are selected based on changes in the physical conditions of the effluent, that is, changes in pressure, temperature, composition, etc. Vessels, heat exchangers and pumping devices are typical points around which a node may be selected. For each node, the design intent and high and low operating limits and design parameters are specified.

In a HAZOP study, the applicable parameters and possibility of deviations are investigated for each node. If a cause can be identified for a deviation, the consequences of occurrence of that cause are established. With the damage mechanism hazard review, this practice is slightly modified. Damage mechanisms and their associated hazards can be identified in the node where the susceptible equipment is addressed. That way, when the team is reviewing a node for damage mechanisms, they are focused on the conditions and operating parameters specific to that node.

3.2 Augmenting the HAZOP Approach

The important aspect of the HAZOP approach that allows for an effective and thorough damage mechanism hazard review is that in a HAZOP, complex systems are broken down into more manageable "nodes". As discussed in Section 3.1, each Node is provided with a standard set of deviations to be reviewed. In our studies, we address damage mechanisms by adding a "Corrosion" or "Damage Mechanism" deviation to the list of parameters and deviations for each node. Other deviations such as "Erosion" and "As Well As Composition" can also be used as a brainstorming tool to identify damage mechanisms.

To address damage mechanisms, personnel with expertise in equipment and pipe metallurgy, inspection, and damage and failure mechanisms are required to participate during these reviews. The typical PHA Team (facilitator, engineering, and operations) will progress through the analysis following the typical HAZOP process. Following the completion of a set of nodes reviewed by the PHA Team, an expanded team that includes personnel with expertise in equipment and pipe inspection, and damage and failure mechanisms will be required to review the damage mechanism portion of the analysis. The set of new personnel may include area inspectors, and plant materials and corrosion experts.

If not already provided as part of the Process Hazard Analysis, the team should request damage mechanism related Process Safety Information (PSI) such as Corrosion Control Plans, inspection history and results, and process metallurgy and corrosion diagrams. These documents provide a starting point for identifying damage mechanisms as part of this robust HAZOP approach.

At this stage of the process, the combined team will review each previously addressed node and focus specifically on the defined Corrosion/Damage Mechanism deviation. There are several benefits of applying this approach. First, during the damage mechanism hazard review the integrated team examines the damage mechanisms by focusing their attention on specific sections of the system. This allows the team to manageably brainstorm damage mechanisms that may occur in the section of the system without broadly analyzing large systems, which in turn requires larger amounts of information for the team to digest. Secondly, because the HAZOP approach relies on identifying deviations from normal operation, it becomes an ideal method for identifying damage mechanisms that may occur or be exacerbated by exceeding normal operating parameters such as temperature, pressure, and composition. Lastly, the primary purpose of a PHA is to identify credible events that may lead to adverse consequences and determine whether appropriate mitigations are in place. As such, including a thorough review of damage mechanisms hazards in a PHA ensures that those related risks are adequately identified and addressed.

3.3 Defining Scenarios - What to Look for?

Identifying damage mechanism related scenarios can be somewhat of a difficult task for a HAZOP Team that has spent a large portion of their discussion reviewing errors or failures that resulted in an immediate or short term noticeable impacts (e.g., inadvertent manipulation of a block valve or a specific pump failing). With damage mechanisms, these types of errors or failures may not be the only initiating events for these damaging conditions.

For an effective review the team must work together to clearly define the operating scenarios, which will be used to assist the materials and corrosion expert in establishing the corrosion mechanisms that may occur. The expert must have a clear understanding of how the process unit is being operated. The operations staff and process engineers are the critical personnel that must relay this information.

The materials and corrosion expert identifies corrosion and damage mechanisms based on a set of categories that can easily be reviewed. The nodes are reviewed to determine if there are hot corrosion mechanisms or cooler ones that may be aqueous. The materials and corrosion expert is also seeking points where chemicals are injected or there are process mixing streams. These points may create additional corrosion concerns due to possible increase in corrosivity within the system, or a thermal differential that may cause thermal fatigue.

Hot Corrosion Mechanisms

If the system is operating hot, the materials and corrosion expert will be looking for a specific set of corrosion or material degradation mechanisms. Hot corrosion mechanisms generally do not result in the pitting type corrosion more commonly found with aqueous corrosion mechanisms. Hot corrosion mechanisms in general cause degradation if the materials of construction are chosen improperly or are operated at excessive temperatures. The corrosion mechanisms at high temperatures typically result in a general wall loss and often result in scaling as in the case of high temperature oxidation. These mechanisms are often of greater concern than the lower temperature aqueous corrosion situations where there is pitting that results in a small leak at the initial failure point.

In addition to high temperature corrosion mechanisms, there are a large number of materials degradation mechanisms. The material degradation mechanisms may not be as easy to inspect for, and may require destructive testing to prove their existence. Typically, there is a time component involved in material degradation. During these events, it is critical that the team establishes the duration of a temperature excursion or abnormal operation.

Some of these material issues do not affect the material while in operation, but change the materials strength and ductility when it is cooled back to near ambient temperature. Based on the findings of the HAZOP, the materials and corrosion expert may recommend adjusting the shutdown and startup of the unit to compensate for loss of the material’s physical properties.

A few examples of these high temperature degradation mechanisms are sulfidation in an environment containing sulfur, high temperature hydrogen attack in a system with hydrogen, and high temperature oxidation in a system which contains oxygen or is open to the atmosphere, sensitization of an austenitic steel, temper embrittlement of low chrome steel, sigma phase embrittlement, and graphitization of carbon steel. The list of mechanisms is quite long and it is important that the materials and corrosion expert understands which mechanisms affect the materials of construction of the equipment in each HAZOP Node. It should be noted that materials may degrade while operating within the design maximum allowable working pressure (MAWP) and the maximum allowable working temperature (MAWT).

Lower Temperature Aqueous Corrosion

Lower temperature aqueous corrosion generally requires free water to be present in the system. The most common cause of these aqueous corrosion mechanisms are oxygen, acids and salts in the free water. While looking at aqueous corrosion mechanisms the corrosion expert must understand chemistry and how these corrodents will affect the materials of construction. While many of these mechanisms result in pits that create small leaks for an initial failure, several of them may result in environmental cracking. Environmental cracking can be a short-term or long-term failure mode depending on the mechanism and the environment. The corrosion expert must understand how severe the environment would be and at what rate the environmental cracking would propagate in the material used in the node. As an example, hot caustic has been known to propagate through an inch of carbon steel within twelve hours and chloride stress corrosion cracking, from rain water at ring joints, has been found where it has not propagated through wall after decades of operation.

While looking for aqueous corrosion mechanisms, it is imperative that the materials and corrosion expert reviews any dead legs including small vents and drains in the system that could collect water and potentially result in concentration of corrodents. It is not uncommon for the dead leg to have significantly worse corrosion than the main piping. In some cases, the piping that is considered a dead leg may actually have a small flow rate due to thermal siphoning. If there is a concern for thermal siphoning, the materials and corrosion expert must review the piping layout to understand if the piping configuration would allow flow and if there is a large enough temperature difference to drive the thermal siphon. Thermal siphons create flow from a hot piping system to a cold one. At the cold end of the system there is an increased risk of salt deposits or water collection. In rare cases in hot systems, the low flow rate in a siphon allows time for thermal cracking and creates a significantly greater corrosion rate in the siphon.

Injection and Mixing Points

Injection and mixing points have two general concerns. The first concern is a thermal differential that could result in thermal fatigue of the piping at, upstream or downstream of the mix point. There are several criteria for looking at these mix points for thermal fatigue related to whether the flow is liquid, gas or vapor. Temperature differences of the two mixing streams that are greater than 200°F for austenitic stainless steels or 300°F for carbon and low alloy steels are of concern and may need additional review. The second concern is that the difference in temperature or stream contents could result in precipitation of more corrosive chemicals, salts or solids that could exacerbate corrosion. In some cases, the mixing of the two streams creates a temperature increase by the heat of mixing which may increase the corrosivity of the fluids or create enough temperature difference for thermal fatigue to occur. Similarly, the mixing of two streams may result in an endothermic reaction that could cool the piping to a temperature where it no longer has good mechanical properties or creates thermal fatigue concerns.

Corrosion Under Insulation (CUI)

The final item in all corrosion reviews is to identify the systems that have insulation. If the system is operating at a temperature below 400°F, corrosion under insulation (CUI) is a concern that must be addressed. The current Nondestructive Examination (NDE) techniques are not particularly good at finding CUI. It is critical that the design and construction is proper and includes a coating under the insulation as well as good moisture barrier outside of the insulation. CUI is the largest cause of leaks in chemical and hydrocarbon processing plants. It is one of the more difficult corrosion mechanisms to find. CUI generally results in pitting and small initial leaks but can cause quite large leaks without early detection.

Microbiologically Induced Corrosion (MIC)

Microbiologically induced corrosion (MIC) is the most difficult corrosion mechanism to identify during a HAZOP and is also one of the most difficult mechanisms to discover with inspection. MIC can occur in many systems and can create rapid failures. Because MIC can attack most materials, it is critical that the materials and corrosion expert explains to the team what conditions are required for the attack in the materials of construction. It is up to the team to help find any locations in the Nodes where these conditions occur.

3.4 Identifying the Initiating Cause of the Damage Mechanism

The PHA Team along with the materials and corrosion expert should review corrosion control plans, corrosion diagrams, and other damage mechanism related PSI as the initial step to identify damage mechanisms. These documents will provide the known damage mechanisms of concern. Identifying existing unknown damage mechanisms will be an imperative task for the team.

To identify other damage mechanisms that may arise, the materials and corrosion expert must have good process information through operations and process engineering support. The materials and corrosion expert will use the information gained through team discussion to determine the damage mechanism initiating causes. The process information is required in order to implement a thorough review and must include process temperatures, pressures, flow rates, and chemical constituents.

In addition to the information regarding normal operations, the process engineer and operations representative must relay information related to abnormal operations and conditions to the team. Abnormal operations that must be considered include startup, shutdown, any anticipated regenerations, regular equipment bypassing or upset conditions. While these abnormal operations do not typically occur over an extended period of time, the effects may be cumulative with some damage mechanisms. An example of a cumulative damage mechanism would be high temperature hydrogen attack (HTHA).

Often, the worst corrosion in a system takes place during the startup and shutdown. While reviewing the nodes, the corrosion expert should explain to the operations and process engineering support what damage could be occurring during these abnormal operations. With this information in mind, operations and process engineering support may be able to change their operation during these abnormal situations to mitigate damage mechanisms.

Care must be taken when identifying the initiating cause of a damage mechanism. When identifying these initiating events, a common method is for the PHA facilitator and team to state the damage mechanism as the cause. For example, teams may state “microbiologically induced corrosion” as the cause. With our reviews, we typically try describe the cause statement in terms of the initiating event(s) or design condition(s) that provide the environment conducive for the damage mechanism to occur. In the case of microbiologically induced corrosion, the initiating events can be issues such as “debris in the cooling water supply laying down in heat exchange tubes” or “loss of biocide injection”. With this approach, the likelihood of the event and the available safeguards can be more clearly established and the team can explore the possibility of implementing inherently safer design.

When identifying initiating causes of damage mechanisms, we have two specific approaches that are followed:

1. Identify deviations from the normal operating conditions (conditions commonly addressed in the HAZOP) and establish damage mechanisms that may occur during these conditions and
2. Identify damage mechanisms that occur due to normal operating conditions or based on system design (e.g., metallurgy, control valves with high pressure drops).

The first approach is to conduct the HAZOP study, paying particular attention to causes that can lead to process upsets or abnormal conditions. Specifically, exceeding design temperatures and pressures and abnormal composition are conditions that should be noted for further review with the materials and/or corrosion expert during the damage mechanism hazard review segments of the analysis.

One such mechanism that provides an example of the first approach is high temperature sulfidation, which to some extent is the corrosion mechanism that initiated California’s drive towards the requirement for Damage Mechanism Reviews. Per API 571 [Reference 6], the three critical factors in the occurrence of high temperature sulfidation are alloy composition, metal temperatures above 500°F, and concentration of corrosive sulfur compounds. Of those factors, the HAZOP process can easily identify specific initiating events that may lead to high temperature conditions. Issues such as loss of reflux to a fractionation tower, increased reboiler firing, or increased feed preheat will be upset conditions addressed during the HAZOP. Additionally, piping material information should readily be available (e.g., information provided on P&IDs and PFDs) as part of the PSI required for PHA. The PHA team, with the expertise of the materials and corrosion expert, should review scenarios such as these and determine if these upset conditions can result in both near and long term corrosion damage. As part of this review, the inspector needs to make sure that the corrosion measurement locations (CML’s) are in the proper location and number to measure the damage.

The second approach is to explore the possibility of damage mechanisms occurring while the system is operating within its acceptable parameters. In these instances, the team must review the physical design of the system, paying particular attention to metallurgy, appurtenances connected to the system, and external conditions to the system. In this approach, the analysis requires the materials and corrosion expert to review the identified node and work closely with the team to discuss any damage mechanisms that may occur. At this time, the operations and engineering representatives will verify whether the condition of the system provides the conducive environment for the identified damage mechanism.

The team should pose questions such as:

- What type of damage mechanisms can occur in this type of environment?
- Is the metallurgy appropriate for this service?
- Has the team experienced or noticed any system conditions of concern?
- Are there deadlegs, CUI, mixpoints, or high pressure drop areas within this node?
- How often do they have to manually drain systems that should be dry?
- Are there damage mechanisms that arise only under specific conditions such as high/low temperature, high/low pressure, or under specific compositional conditions? If so, can this system provide those conditions during normal and abnormal operations?

A damage mechanism that provides an example of the second approach is Corrosion Under Insulation (CUI). This damage mechanism does not result directly from an abnormal process condition, but is rather influenced by external conditions to the system. The initiating cause can be stated in terms of "damaged insulation due to external causes" or "excessive rainfall" as examples. Figure 1 provides sample initiating events written on a typical HAZOP worksheet.

Figure 1 - Sample Cause Statements

Node:	1. Fractionation Tower, including overhead vapors to the Overhead Accumulator	
Deviation:	14. Corrosion	
Causes	**CAT**	**Consequences**
1. Debris in the cooling water supply to the Overhead condensers due to issues at the Cooling Tower	EXT	
2. Carbon steel equipment at the bottom of the Fractionation Tower	NOR	
3. Damaged insulation on the Fractionation Tower overhead piping due to external causes	EXT	

3.5 Establishing Consequence and Risk Ranking

Consequences are the result of the deviation cause and may be expressed in terms of system condition, release of materials, effects on other equipment, deterioration of equipment, adverse effects on workers and the public, etc. When expressing the consequences of a deviation, no limits are imposed in terms of location and area. Consequence discussions are carried out until all possible adverse conditions are identified. Also, when discussing potential consequences, no credit is given to the mitigative impact of the available safeguards. This practice allows the analysts to identify the worst possible consequence level that is needed to create a common basis for establishing the risk ranking of each scenario.

Postulating and documenting the consequence of a damage mechanism follows the same approach used during the HAZOP with one special consideration: the end result of a damage mechanism may require a longer amount of time to become evident than other process upset conditions. For example, a damage mechanism may require months or years under a specific condition to result in a through-wall failure. Resultantly, the facilitator must be cautious in establishing the final consequence and must drive the discussion to determine whether there is a reasonable potential for the damage mechanism to reach the worst-case consequence (i.e., loss of containment event or significant asset damage). The facilitator should ensure that both the damage mechanisms with short term, as well as long term damage are discussed as part of these analyses. Figure 2 provides a flow chart that can be used to establish whether a damage mechanism consequence should be postulated as a loss of containment event.

In terms of the HAZOP style for stating the consequence, the team must identify any initiating factors resulting from the cause that leads to the damage mechanism, then identify the damage mechanism, and finally identify the worst credible result of the damage mechanism in terms of the failure size and release potential. In these instances, we suggest being thorough in the documentation and provide all enabling conditions of the event as part of the consequence statement and/or as a remark for the scenario.

The team, with the guidance of the materials and corrosion expert, should identify the failure in terms of expected failure size (e.g., pinhole leak, fish mouth failure, brittle fracture, crack, etc.). As stated above, specific care must be taken to establish a realistic consequence since many damage mechanisms do not immediately result in loss of containment events. Several factors that play into this determination are the following:

- Type of and aggressiveness of the damage mechanism
- Frequency of the initiating cause and acceptable allowance for recurrence of the cause
- Existing wall thickness of affected equipment (will the thinning wall last until the next scheduled inspection?)
- Existing and type of maintenance inspections (will the type of inspection method identify the thinning condition and measure it while online?)

In addition, consideration should also be given to the pressure, temperature, and composition of the released material. All of these factors will affect the ultimate consequence severity of the event. For example, a pinhole leak in a system that is at 5 psig will have a different effect that a pinhole leak in a system at 500 psig. In addition, a pinhole leak of sour water will have a different consequence than a release of sour hydrocarbon gas. It must be noted that damage mechanisms that crack or can create catastrophic failures are generally not accepted by the materials and

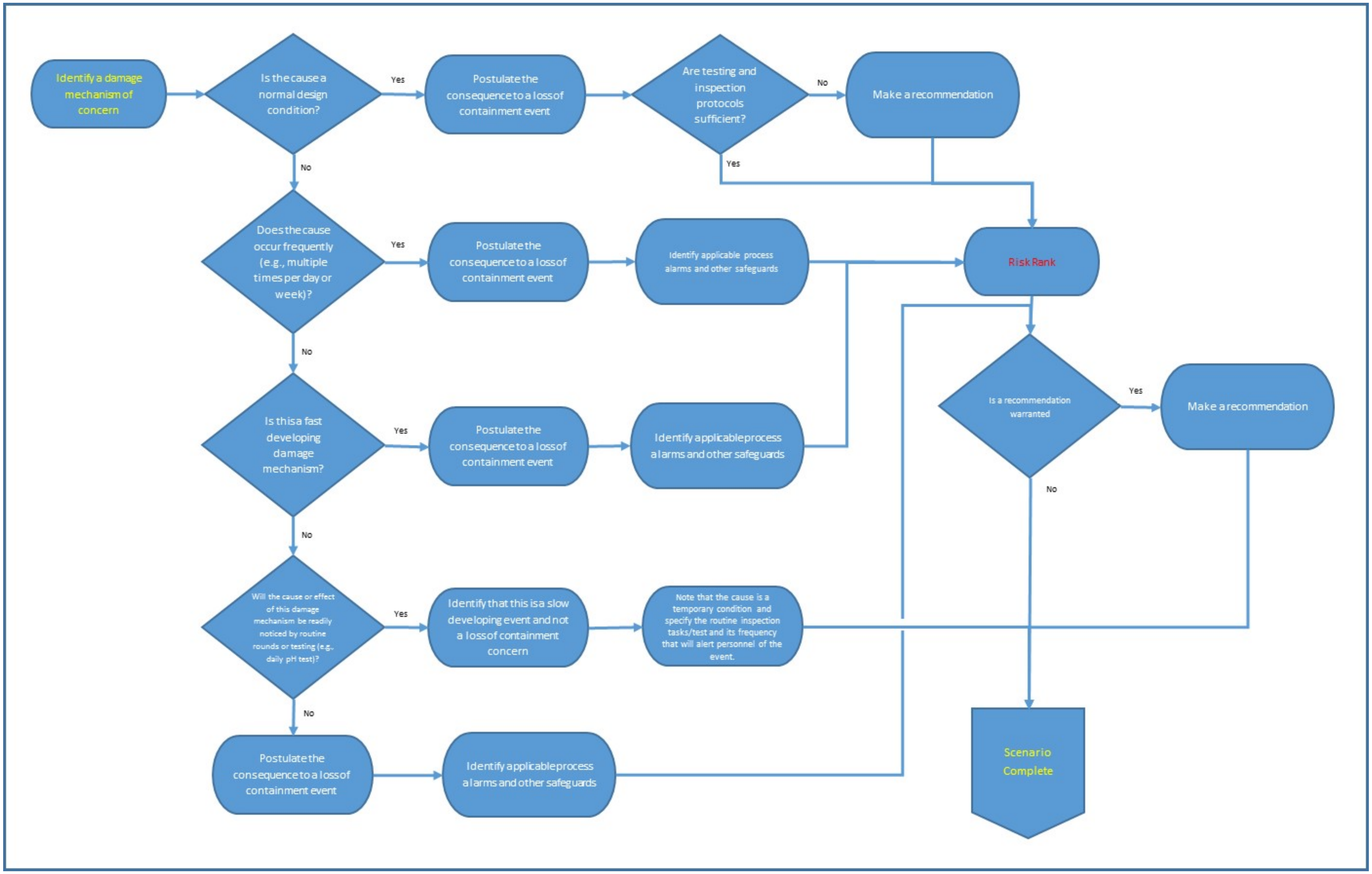

Figure 2 - Damage Mechanism Consequence Flow Chart

corrosion expert during the design. If credible damage mechanisms that create cracking or catastrophic failures are found during the HAZOP, a recommendation should be made to mitigate the initiating cause or to change the material of construction.

It is the PHA Team's responsibility to identify the appropriate consequence of the damage mechanism under review. An accurate consequence will assist in determining whether additional protective measures are required. Figure 3 provides an example of the consequence structure.

Figure 3 - Sample Consequence Statements

Node: 1. Fractionation Tower, including overhead vapors to the Overhead Accumulator

Deviation: 14. Corrosion

Causes	CAT	Consequences	CAT
1. Debris in the cooling water supply to the Overhead condensers due to issues at the Cooling Tower	EXT	1. Potential for laydown of debris in the cooling water side of the Overhead Condensers, resulting in reduced cooling water flow. Potential for microbiologically induced corrosion (MIC) due to reduced flow and poor contact with biocide. Potential for pitting corrosion in the cooling water side leading to a pinhole leak. Potential for tube failure. Potential for release of water into the process side. Potential for operational upset at the Overhead Exchanger.	AS
2. Carbon steel equipment at the bottom of the Fractionation Tower	NOR	1. Potential for high temperature sulfidation at the bottom of the Fractionation tower and bottoms piping. Potential for a long term corrosion concern. Potential for eventual fish mouth failure leading to a significant release of liquid hydrocarbons into the area. Potential for fire. Potential for personnel exposure.	PE O
3. Damaged insulation on the Fractionation Tower overhead piping due to external causes	EXT	1. Potential for water intrusion underneath the damaged insulation. Potential for pitting leading to an eventual pinhole leak. Potential for a release of sour gas in the area well above grade. Potential for personnel exposure to sour gas.	PE O

3.6 Defining safeguards

Damage mechanism scenarios will have a variety of safeguards that will be unique to the specific damage mechanism and will deviate from the normal HAZOP approach of identifying safeguards. The identified safeguards will be in terms of process upset detection (alarms), inspection and testing types and frequencies, and personnel observation (i.e., during operator rounds).

As discussed earlier, damage mechanisms can occur either due to a process upset condition (e.g., high/low temperature or pressure) or can be expected to occur due to current process design and equipment conditions. For the former cases, the PHA team should identify any alarms that may alert personnel to conditions susceptible to a specific damage mechanism. For example, high temperature alarms and their appropriate set points may be noted as detective safeguards against High Temperature Hydrogen Attack or material creep.

For damage mechanisms of the latter form, the PHA Team must determine the type and frequency of the inspection protocol and should only identify these actions as safeguards if they are part of current facility practices. The adequacy of inspection and testing practices must take into consideration previous inspection/testing results, current expected equipment wall thickness and calculated corrosion rate. The review of the inspection adequacy may require outside expertise when inspecting for specific damage mechanisms that require specialized inspection techniques. Otherwise, a recommendation should be generated (see Section 3.3.4 below).

The PHA Team should discuss the following questions:

- What type of inspection techniques are used?
- Do these inspection techniques follow industry guidelines for equipment in this type of service?
- Is there sufficient wall thickness to last until the next scheduled inspection?
- Are there any upset conditions that may worsen the effect of this damage mechanism? If so, are there detective devices and written responses to these upsets?

Figure 4 provides an example of safeguards identified during a HAZOP.

Figure 4 - Sample Safeguards

Node: 1. Fractionation Tower, including overhead vapors to the Overhead Accumulator

Deviation: 14. Corrosion

Causes	CAT	Consequences	CAT	Safeguards
1. Debris in the cooling water supply to the Overhead condensers due to issues at the Cooling Tower	EXT	1. Potential for laydown of debris in the cooling water side of the Overhead Condensers, resulting in reduced cooling water flow. Potential for microbiologically induced corrosion (MIC) due to reduced flow and poor contact with biocide. Potential for pitting corrosion in the cooling water side leading to a pinhole leak. Potential for tube failure. Potential for release of water into the process side. Potential for operational upset at the Overhead Exchanger.	AS	1. Strainer at the cooling water supply pumps 2. FI-123 provides low flow alarm on the cooling water supply to the Overhead Condensers 3. Overhead Condensers are removed from service and internally inspected once per Turnaround (3 year cycle)
2. Carbon steel equipment at the bottom of the Fractionation Tower	NOR	1. Potential for high temperature sulfidation at the bottom of the Fractionation tower and bottoms piping. Potential for a long term corrosion concern. Potential for eventual fish mouth failure leading to a significant release of liquid hydrocarbons into the area. Potential for fire. Potential for personnel exposure.	PEO	1. TI-456 provides a high temperature alarm at 450F at the bottom of the Fractionation Tower 2. Ultrasonic thickness measurements and profile radiography of the Fractionation Tower bottom and bottoms piping once per Turnaround (3 year cycle) 3. Corrosion probes provided at various locations on the Fractionation Tower bottoms will provide real-time data on wall thickness.
3. Damaged insulation on the Fractionation Tower overhead piping due to external causes	EXT	1. Potential for water intrusion underneath the damaged insulation. Potential for pitting leading to an eventual pinhole leak. Potential for a release of sour gas in the area well above grade. Potential for personnel exposure to sour gas.	PEO	1. Operator daily rounds include inspections for evidence of water intrusion and damaged insulation or leaks. 2. Neutron backscatter of piping and equipment once per turnaround (3 year cycle) identified as susceptible to CUI

3.7 Considering Recommendations

As it is typically practiced in a HAZOP study, a recommendation must be generated if the scenario risk ranking demonstrates an unacceptable risk per the facility's risk ranking matrix. Recommendations may also be generated if there is team consensus that modifications to the system's mechanical integrity program or additional system modifications are warranted. The facilitator should also discuss the possibility of equipment replacement with improved metallurgy or internal cladding as potential recommendations (inherently safer design). Additionally, recommendations must be made if there are any conditions (e.g., maintenance practice or equipment metallurgy) that do not meet current site or industry standards (RAGAGEP).

4. Team Composition and Associated Roles and Responsibilities

4.1 PHA Facilitator's Role

The facilitator's role is to guide the discussion using a standard and consistent methodology and ensure that there is detailed documentation of the discussion. In these analyses, the facilitator should also ensure that the team is following a consistent approach when discussing the damage mechanism and identifying the worst-case consequence. It is the facilitator's role to challenge the team to identify the worst credible case scenario to ensure that a thorough and accurate analysis is performed. Ideally, the facilitator should record as much information as possible on the HAZOP worksheets such that the basis for the consequence, risk ranking, and safeguards are provided. This may include information such as expected rate of corrosion and conditions that may increase the corrosion rate or effects of the damage mechanism.

4.2 PHA Team's Role

The PHA Team provides the documents and knowledge that define the engineering and operational aspects of the process. The PHA Team's role is to assist in establishing the initiating cause and the ultimate consequence of the postulated scenario. It is the responsibility of the PHA team (operations and engineering) to identify the process upset condition that can lead to higher corrosion potential in the system. In addition, the PHA team must establish the worst-case consequence and determine the appropriate risk ranking for the scenario.

Additionally, the PHA Team should note any unique or abnormal corrosion issues that have been observed. PHAs allow for members of engineering and operations to voice any observed concerns and receive an appropriate response for those identified issues. This may include any observed external corrosion on equipment, potential process deadlegs and mixpoints (injection points), cavitation heard in the system, abnormal levels of fouling in the system and upset conditions that may result in damage mechanisms identified by the corrosion expert.

4.3 Materials and Corrosion Expert's Role

When reviewing damage mechanisms as part of PHAs, the materials and corrosion expert plays the crucial role of identifying the damage mechanisms that may affect the system. The materials and corrosion expert provides the materials, corrosion and inspection experience. The materials and corrosion expert must understand all of the corrosion mechanisms that would be present within the reviewed process. They must also be an expert in the materials of construction that would normally be used for the process unit. In addition, the materials and corrosion expert must have an understanding of Nondestructive Evaluation (NDE) methods that would be used for detection of corrosion mechanisms in the materials of construction for the unit. Lastly, the corrosion expert will assist the team in consequence determination, identification of appropriate safeguards, and risk ranking scenarios.

Figure 5 - Team Responsibilities in the Context of Damage Mechanism Hazard Reviews

PHA Facilitator

1. Lead the HAZOP discussion
2. Ensure the Corrosion Expert receives and provides needed information
3. Ensure the HAZOP method is applied properly and documented consistently.

PHA Team
Engineering and

1. Provide operating conditions
2. Identify process upset conditions
3. Establish the consequence severity based on the type of failure, released material and process conditions
4. Establish the likelihood based on the estimated time until failure
5. Identify abnormal system conditions

Materials and Corrosion Expert

1. Identify known damage mechanisms of concern.
2. Establish the type of failure that may occur.
3. Provide an estimated time frame until loss of containment
4. Identify appropriate safeguards
5. Respond to concerns by the team.
6. Propose recommendations when deemed necessary

5. Sample HAZOP Corrosion Scenarios

Damage mechanism hazards can easily be addressed using a standard HAZOP worksheet. The HAZOP worksheet provides an easy means to fluidly review both process upset conditions and damage mechanisms. Figure 6 provides a sample PHA worksheet taken from a recent study.

Figure 6 - Sample PHA Worksheet

Node: 1. Fractionation Tower, including overhead vapors to the Overhead Accumulator

Deviation: 14. Corrosion

Causes	CAT	Consequences	CAT	Safeguards	S	L	RR	HAZOP Recommendations	Comments
1. Debris in the cooling water supply to the Overhead condensers due to issues at the Cooling Tower	EXT	1. Potential for laydown of debris in the cooling water side of the Overhead Condensers, resulting in reduced cooling water flow. Potential for microbiologically induced corrosion (MIC) due to reduced flow and poor contact with biocide. Potential for pitting corrosion in the cooling water side leading to a pinhole leak. Potential for tube failure. Potential for release of water into the process side. Potential for operational upset at the Overhead Exchanger.	AS	1. Strainer at the cooling water supply pumps 2. FI-123 provides low flow alarm on the cooling water supply to the Overhead Condensers 3. Overhead Condensers are removed from service and internally inspected once per Turnaround (3 year cycle)	1	C - 10^{-3}	Low Risk		1. 2015 PHA - Per API 571, low flow conditions allow for the growth of microorganisms.
2. Carbon steel equipment at the bottom of the Fractionation Tower	NOR	1. Potential for high temperature sulfidation at the bottom of the Fractionation tower and bottoms piping. Potential for a long term corrosion concern. Potential for eventual fish mouth failure leading to a significant release of liquid hydrocarbons into the area. Potential for fire. Potential for personnel exposure.	PEO	1. TI-456 provides a high temperature alarm at 450F at the bottom of the Fractionation Tower 2. Ultrasonic thickness measurements and profile radiography of the Fractionation Tower bottom and bottoms piping once per Turnaround (3 year cycle) 3. Corrosion probes provided at various locations on the Fractionation Tower bottoms will provide real-time data on wall thickness.	4	C - 10^{-3}	High Risk	1. 2015 PHA Reval - Upgrade the piping at the bottom of the fractionation tower to a chromium content material to reduce the potential for high temperature sulfidation at the bottom of the tower.	1. 2015 PHA - Sulfidation of iron-based alloys usually begins at metal temperatures about 500F. 2. 2015 PHA Reval - Increasing chromium content of the material significantly increases resistance to high temperature sulfidation.
3. Damaged insulation on the Fractionation Tower overhead piping due to external causes	EXT	1. Potential for water intrusion underneath the damaged insulation. Potential for pitting leading to an eventual pinhole leak. Potential for a release of sour gas in the area well above grade. Potential for personnel exposure to sour gas.	PEO	1. Operator daily rounds include inspections for evidence of water intrusion and damaged insulation or leaks. 2. Neutron backscatter of piping and equipment once per turnaround (3 year cycle) identified as susceptible to CUI	3	D - 10^{-4}	Moderate		1. 2015 PHA Reval - CUI affects piping that operate at temperatures below 350F for carbon and low alloy steels.

6. Proposed California PSM and CalARP Requirements

The Damage Mechanism Review clause of the proposed CalARP and California PSM regulations [References 4 and 5] include many similarities to the requirements established in the Process Hazard Analysis section of those regulations. Similarities include the requirement that the analysis be revalidated on a 5-year cycle, the analysis must be performed by a team with the necessary expertise, reports must be retained for the life of the system, and the analysis must include methods to prevent or mitigate damage (safeguards). With these similarities, the PHA naturally can become an initial starting point to ensure a thorough review of damage mechanisms hazards. The discussed approach provides a systematic and thorough method for addressing damage mechanism related hazards. At this moment, the requirement for Damage Mechanism Reviews will only apply to California refineries, but many other types of chemical process facilities are susceptible to damage mechanisms. Therefore, part of a facility's risk reduction philosophy should include a thorough discussion of damage mechanisms as part of the PHA process.

7. Conclusion

In the chemical process industry, the occurrence of damage mechanisms on process equipment is unavoidable, but can be mitigated through improved metallurgy, positive identification (inspection and testing), and proper control of operating conditions. Hazard reviews are completed for known mechanisms under known operating conditions. While we readily review what is known, it is the unknown that has caused many of industries worst failures.

The first step to mitigating the effects of damage mechanisms is proper identification of these mechanisms and establishing the risk levels of such conditions. As such, the Process Hazard Analysis (specifically Guide-Word Style HAZOP approach) required as part of the Risk Management Plan and Process Safety Management regulations provides an effective means to identify damage mechanisms, establishes their effect (consequences), verifies appropriateness and availability of safety measures, and assists in identifying effective risk reduction measures.

References

1. "Investigation Report - Catastrophic Rupture of Heat Exchanger (Seven Fatalities) - Tesoro Anacortes Refinery - Anacortes, Washington, April 2010" U.S. Chemical Safety and Hazard Investigation Board, Report 2010-08-I-WA, May 2014.

2. "Final Investigation Report – Chevron Richmond Refinery – Pipe Rupture and Fire - Chevron Richmond Refinery #4 Crude Unit – Richmond, California, August 6, 2012" U.S. Chemical Safety and Hazard Investigation Board, Report 2012-03-I-CA, January 2015.

3. "Improving Public and Worker Safety at Oil Refineries", Report of the Interagency Working Group on Refinery Safety, California Environmental Protection Agency, February 2014

4. *"California Accidental Release Prevention (CalARP) Program"*, Title 19 of CCR Division 2, Chapter 4.5.

5. *"Process Safety Management of Highly Hazardous Materials (PSM)"*, Cal/OSHA's California Code of Regulations, Title 8, §5189.

6. "Damage Mechanisms Affecting Fixed Equipment in the Refining Industry", American Petroleum Institute, API Recommended Practice 571, Second Edition, April 2011

7. "Risk Management Programs for Chemical Accidental Release Prevention," U.S. Environmental Protection Administration, 40 CFR Part 68.

8. "Guidelines for Hazard Evaluation Procedures", published by the Center for Chemical Process Safety of the American Institute of Chemical Engineers, 3rd Edition, April 2008.